

# Fatty Peroxides: Synthesis, Analysis, and Reactions<sup>1</sup>

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PEROXIDES are a natural class of functional compounds to be explored by lipid chemists. Rancidity of food oils and oxidative-polymerization of oil-based paints result from initial peroxide formation. Industrial applications and laboratory reactions of peroxides have rapidly expanded to offer chemurgic opportunities for lipid peroxides as intermediates for other useful chemicals. There is also evidence that lipid peroxides may participate in radiobiological damage (2), in cancer (3,4), and in aging (5). In view of these varied developments in peroxide chemistry, a short course of this nature can only survey the subject in a cursory fashion, but lipid chemists should be aware of some of the major methods for synthesizing peroxides, of some useful analytical methods, and of a few intriguing reactions involving peroxides to highlight their utility.

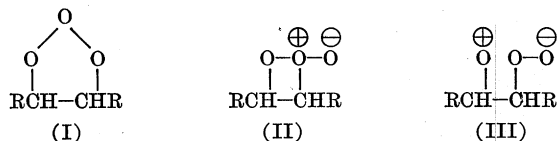
## Types and Structures

Organic peroxides are considered to be derivatives of hydrogen peroxide in which one or both hydrogen atoms may be replaced by organic radicals. The peroxide function consists of two oxygen atoms directly linked to one another by single bonds. Formally, any classical organic compound may be converted to a peroxide by inclusion of the O—O linkage. The following classification (Table I), illustrates relationships between peroxides and their non-peroxy analogs.

The R groups may be aliphatic (primary, secondary, tertiary, cyclic), alicyclic, aromatic, steroidal, heterocyclic, or organometallic (including elements other than carbon).

No "true" aromatic peroxide containing the O—O group directly attached to the aromatic ring system, such as diphenyl peroxide ( $C_6H_5O-OC_6H_5$ ), has ever been isolated, although some claims to the existence and attempts in the preparation of this type have been made (6,7,8). All known aromatic peroxides have one or more atoms between the peroxy group and the aromatic ring.

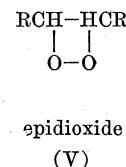
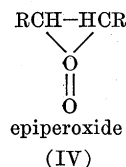
Ozonides may be considered to be a special class of peroxy compounds. Ozonization of unsaturated hydrocarbons and fats is stated to form a primary "molozonide" (9) (Table I) which is rapidly converted to the ozonide (or iso-ozonide) (9) (Table I). The following three possible structures for molozonide which include zwitterion structures have been suggested (9).



Direct addition of oxygen to a double bond to form a "moloxide" has been proposed in some autoxidation theories to account for some of the products. Staudinger proposed a rearrangement of the initial adduct to a cyclic peroxide (10). The first of the moloxide structures has been termed the "epiperoxide

of Paquot" and the second of these the "epidioxide of Staudinger" (11).

These intermediates have never been isolated.



Among inorganic peroxides there exists a highly reactive, paramagnetic class designated as superperoxides, for example, potassium superperoxide ( $KO_2$ ). The protic analog, hydroperoxy or perhydroxyl radical ( $HOO\cdot$ ) has been referred to as hydrogen superoxide (12), but the alkyl peroxy radical ( $ROO\cdot$ ), also paramagnetic, has not generally been designated under the superperoxide classification.

## Synthesis

### Hydroperoxides

Alkyl hydroperoxides, the simplest organic peroxides structurally related to hydrogen peroxide, are produced by the following general methods: (1) autoxidation of the hydrocarbons RH or fat and oil derivatives with molecular oxygen; (2) oxidation of organometallic compounds; (3) alkylation of hydrogen peroxide with alkylating agents like alkyl sulfonates, sulfates, halides, and alcohols in the presence of alkali or acid. Ozonization of olefins leads to hydroperoxide derivatives of the ketal and related types but this is not a synthetic method for simple aliphatic hydroperoxides.

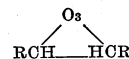
### Hydroperoxides by Autoxidation of Hydrocarbons and Fats

Autoxidation, defined as the spontaneous reaction between atmospheric oxygen and organic compounds,

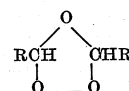
TABLE I  
Nomenclature and Structures of Peroxides and Non-Peroxy Analogs

Hydroperoxide.....	ROOH	Alcohol	ROH
Dialkyl peroxide.....	ROOR	Ether	ROR
Peroxy acid, peracid or acyl hydroperoxide.....	$\begin{array}{c} RC-OOH \\    \\ O \end{array}$	Acid	$\begin{array}{c} RCOH \\    \\ O \end{array}$
Peroxy ester or perester.....	$\begin{array}{c} RC-OOR \\    \\ O \end{array}$	Ester	$\begin{array}{c} RCOR \\    \\ O \end{array}$
Diacyl peroxide (aliphatic).....	$\begin{array}{c} RC-OO-CR \\    \quad    \\ O \quad O \end{array}$	Anhydride	$\begin{array}{c} RC-O-CR \\    \quad    \\ O \quad O \end{array}$
Diaryl peroxide (aromatic).....			
Peroxy derivatives of aldehydes and ketones.....	$\begin{array}{c} R \\   \\ C-OH \\   \\ OOH \\   \\ R \end{array}$	Hydrated form of aldehydes and ketones	$\begin{array}{c} R \\   \\ C-OH \\   \\ R \end{array}$

Ozonides  
Primary ozonide (molozonide—see text)



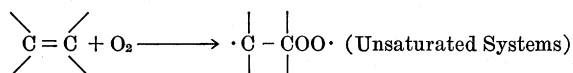
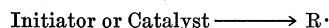
Ozonide or iso-ozonide



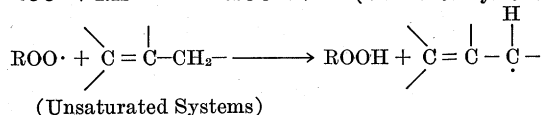
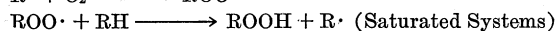
<sup>1</sup> Eastern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

occurs under mild conditions, although light, heat, the concentration of oxygen, moisture, and the presence of catalysts or inhibitors appear to affect the reaction with different results. Because of the di-radical nature of oxygen, the majority of these reactions, excluding some photochemical or organometallic oxidations, proceed through a free radical chain process. Autoxidation may be described by the following sequence of reactions (10,13,64).

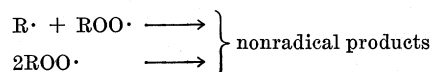
#### Chain Initiation



#### Propagation



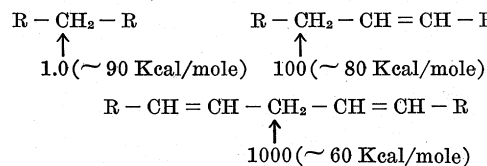
#### Termination



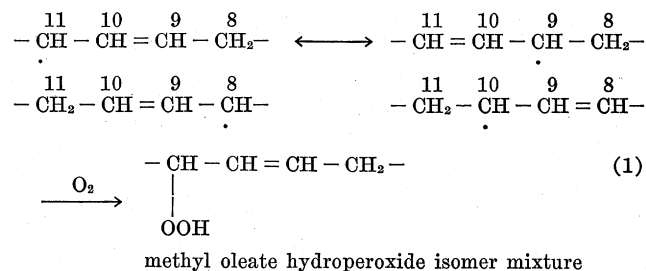
The initiator may be a peroxide or azo compound that decomposes to free radicals or it may be the substrate itself that is converted or excited to free radicals by catalysts, light, heat or chemical methods. The initial free radical oxidizes to a peroxy radical which abstracts hydrogen from hydrocarbon to form hydroperoxide. A free radical is regenerated and a propagation cycle established. Interaction of free radicals to give nonradical products terminates the chain. The order of reactivity of hydrogen atoms attached to carbon is tertiary > secondary > primary. Autoxidation often permits good yields of hydroperoxides from a tertiary carbon-hydrogen bond and poor yields from a primary one. A classical example of the utility of autoxidation is the production of cumene hydroperoxide as an intermediate in one industrial manufacturing process for phenol and acetone.

In unsaturated systems, initiation may occur by direct addition of oxygen to the double bond. This addition reaction occurs only in trace amounts, for the main propagative attack occurs at C-H alpha to the double bond. Furthermore, the oxidation rates for unsaturated systems, such as those found in most fats and oils, are higher than for saturated systems. The allylic radical formed is resonance-stabilized. The importance of resonance stabilization in the oxidation of fats is indicated by the relative reactivities of methyl stearate, oleate, and linoleate toward a peroxy radical. One double bond alpha to a methylene increases the rate 100-fold and a further 10-fold increase occurs with two similarly situated double bonds (14,15).

#### Relative Reactivity (and Bond Dissociation Energy)



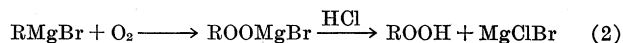
The bond dissociation energy which is a measure of the carbon-hydrogen bond strength decreases with allylic activation paralleling the relative reactivity. Oxidation of the alpha methylene produces a resonance-stabilized allylic radical with cis-trans isomerization, i.e.



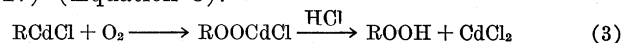
Such isomerization is responsible for at least four pairs of cis-trans isomers present in the methyl oleate hydroperoxide which might be isolated from the autoxidized ester (10). Autoxidations of unsaturated fatty esters cannot be expected to yield pure singularly-defined peroxides, although one or two of these may predominate in the mixture.

#### Hydroperoxides by Organometallic Oxidations

Organometallic compounds autoxidize to peroxide intermediates. Sanderson (16) compiled a table in which he correlated the reactivities of 34 methyl-element compounds of the type,  $\text{E}(\text{CH}_3)_n$ , where E represents an element of the periodic table and n the number of attached methyl groups. His correlation suggests the feasibility of oxidizing several such alkyl derivatives to peroxy intermediates. Walling and Buckler (7) successfully prepared hydroperoxides by oxidation of Grignard derivatives at  $-70^\circ\text{C}$  in ether solutions (Equation 2).

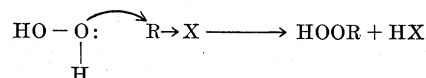


At higher temp the Grignard reduces the intermediate organometallic peroxide to an alcoholate. Cadmium and zinc alkyls undergo this latter undesirable reaction less readily than do Grignard reagents. Because they are also less reactive to carboxylation and hydrolysis (16) than are Grignard reagents, they appear to be superior organometallic intermediates for oxidation to hydroperoxides. Autoxidation of the cadmium alkyls has since been used to prepare hydroperoxides up to octyl hydroperoxide in 90% yields (17) (Equation 3).

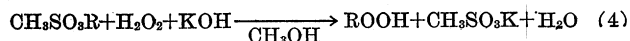


#### Hydroperoxides by Alkylation of Hydrogen Peroxide

**Nucleophilic Substitutions in Alkaline Media.** Electronegative groups ( $-\text{X}$ ), like sulfonate or halide, polarize the adjacent carbon atom to permit attack by the electron-donating hydrogen peroxide or hydroperoxide anion.

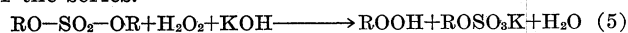


**Use of Alkyl Methanesulfonate:** Perhydrolysis of alkyl methanesulfonates has been used to prepare n-alkyl hydroperoxides up to n-octadecyl hydroperoxide (18,19) and sec-alkyl hydroperoxides up to 2-octyl hydroperoxide (20).



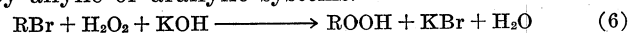
The method is limited by the low solubility of long-chain alkyl methanesulfonates and the long reaction times required in the basic medium so that peroxide decomposition proceeds at a significant rate to result in poor yields of long-chain derivatives.

Use of Dialkyl Sulfate: Perhydrolysis of dialkyl sulfates is limited to the first three or four members of the series.



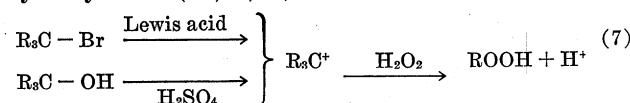
Only half of the molecule is convertible to peroxide. The resulting half-alkyl sulfate salt resists further hydrolysis, even in boiling solution (21,22,23).

Use of Alkyl Halides: Chlorides and bromides are readily perhydrolyzed when the halogen is activated by allylic or arallylic systems.



The halides are less satisfactory reactants than methanesulfonates for preparing saturated primary and secondary hydroperoxides.

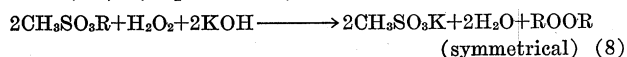
**Carbonium Ion Substitutions in Acid Media.** Acid-catalyzed procedures work well for substituents on tertiary carbons or on carbon atoms activated by allylic systems (24,25,26).



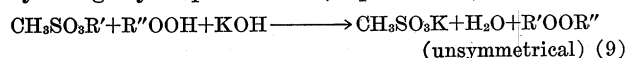
The carbonium ion intermediates,  $\text{R}_3\text{C}^+$ , are then attacked by the hydrogen peroxide nucleophile. The method is less suitable for the synthesis of aliphatic primary and secondary hydroperoxides.

#### Dialkyl Peroxides

The synthesis of dialkyl peroxides is considered to be an extension of hydroperoxide synthesis. Perhydrolysis of alkyl methanesulfonate appears to be the most useful method for this peroxide class requiring two moles of alkylating reactant/mole of hydrogen peroxide. Dialkyl peroxides up to seven carbons/alkyl chain have been described for the aliphatic series (27) (Equation 8).



Unsymmetrical dialkyl peroxides can be obtained by alkylating hydroperoxides (Equation 9).

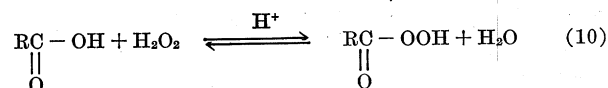


#### Peroxy Acids

Approximately twenty methods and modifications are available for peroxy acid synthesis. The methods reported here are of major importance.

##### *Acylation of Hydrogen Peroxide in Acid Media*

Formation of a peroxy acid from the parent acid and hydrogen peroxide is an equilibrium process whose rate of formation is acid-catalyzed (28).

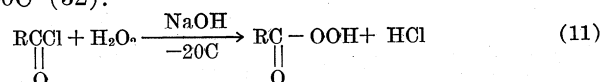


Azeotropic distillation of the water with lower aliphatic esters (i.e. ethyl acetate) completes this reaction in accordance with the Mass Law. This method is limited to the first few members of an aliphatic series and fails to produce long-chain derivatives (29).

Use of concentrated sulfuric acid as a solvent-catalyst and 60% hydrogen peroxide permits high conversions of fatty acids and their esters to peroxy acids (30). This method is unsatisfactory for very long chains like stearic acid and fails to convert aromatic acids to their corresponding peroxy acids. Use of methanesulfonic acid as a solvent-catalyst and 90% strength hydrogen peroxide permits nearly quantitative conversions of both aliphatic and aromatic acids to peroxy acids (31). This latter method is nearly general in scope while also offering a convenient method for preparing very strong peroxy acids as new oxidizing reagents for unsaturated fatty acid systems hitherto epoxidized with difficulty.

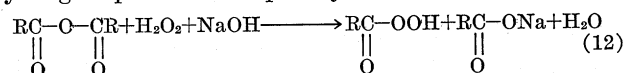
##### *Acylation of Hydrogen Peroxide in Alkaline Media*

**Acid Chlorides:** Acid chlorides react with alkaline hydrogen peroxide in tetrahydrofuran solution at  $-20^\circ\text{C}$  (32).



Precipitation of peroxy salts minimizes further acylation to diacyl peroxides. This method is satisfactory for strong acids like p-nitrobenzoic acid but is inefficient for the weaker aliphatic acids.

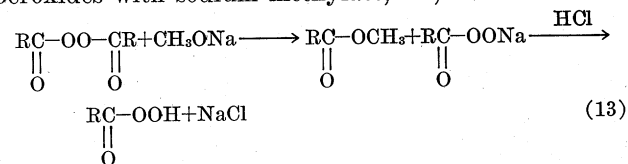
**Anhydrides:** Anhydrides can be used for acylating hydrogen peroxide to peroxy acids.



Because only half of the anhydride molecule forms peroxy acid and the remaining moiety is neutralized to the parent acid salt, yields from linear anhydrides are low and the derived peroxy acids difficult to purify. Hence, this method is more useful for converting cyclic anhydrides to monoperoxy acids than for similar conversions of linear anhydrides (Equation 12).

##### *Diacyl Peroxide Hydrolysis*

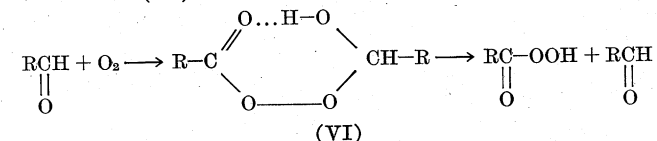
The classical procedure (33) of reacting diacyl peroxides with sodium methylate, i.e.,



the only general one until recently (31,32) is somewhat difficult to perform in practice and often gives poor yields. It has, nevertheless, been the principal procedure by which chemists could prepare an extensive variety of peroxy acids in the aromatic series.

##### *Aldehyde Oxidation*

Perbenzoic acid has been prepared by benzaldehyde oxidation (34).

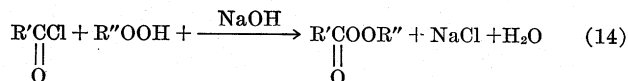


Air oxidation of acetaldehyde has recently been developed into an efficient industrial process for peracetic acid (35). The intermediate unstable peroxide,

$\alpha$ -hydroxyethyl peracetate [structure (VI) where R = CH<sub>3</sub>], that forms in this oxidation has been isolated and characterized (36).

#### Peroxy Esters

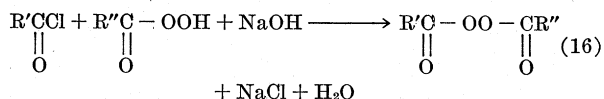
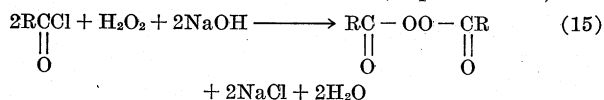
Acylation of hydroperoxides through use of a Schotten-Bauman type of reaction is a standard technique for peroxy ester synthesis. Aqueous alkali is usually used as the acid neutralizer.



However, pyridine as acid acceptor in laboratory preparations of long-chain fatty peroxy esters avoids emulsion difficulties that arise from alkaline hydrolysis with some attendant soap formation, and gives quantitative yields of peresters. *t*-Butyl peresters prepared from fatty acids up to 18 carbons have been obtained by the pyridine method (37).

#### Diacyl Peroxides

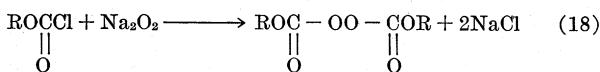
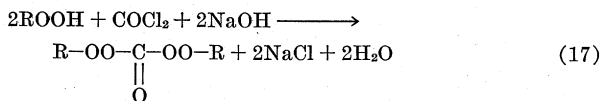
Acylation of hydrogen peroxide and peroxy acids is a useful synthesis for symmetrical diacyl peroxides from the former (Equation 15) and unsymmetrical diacyl peroxides from the latter (Equation 16).



The method is applicable to both aliphatic and aromatic derivatives. Pyridine is a preferred acid acceptor for laboratory preparations of the long chain derivatives (37). Diacyl peroxides having up to 18 carbons/chain have been prepared (37,38).

#### Peroxy Carbonates

Peroxy carbonates may be derivatives of either the peroxy ester (Equation 17) or the diacyl peroxide class (Equation 18).

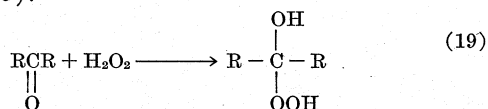


The former peroxy ester type has -O-O- between alkyl and carbonyl; the latter diacyl peroxide type bears the -O-O- between two carbonyls (39).

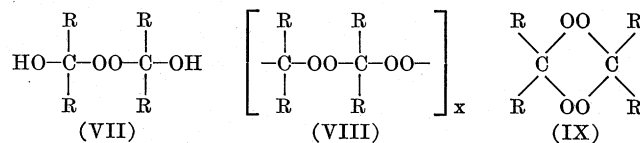
#### Peroxy Derivatives of Aldehydes, Ketones and Related Types

##### Reaction of Aldehydes and Ketones with Hydrogen Peroxide

Reaction of aldehydes and ketones with hydrogen peroxide in non-aqueous solvents such as ether, lead to a wide range of aldehyde and ketone peroxide types. The initial reaction forms the monohydroperoxy analog of the aldehyde or ketone hydrate (Equation 19).



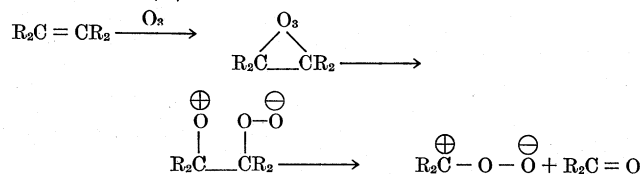
Further condensation to bishydroxyalkyl peroxides (VII) or chain (VIII) and ring (IX) forms of polyalkylidene peroxide may occur in aqueous media or by



acid catalysis. Condensation of aldehydes and ketones with hydroperoxides instead of hydrogen peroxide results in many obvious extensions to this type of peroxy derivative.

##### Ozonization of Olefins

Ozone addition to a double bond forms an unstable molozonide that cleaves to a zwitterion and an aldehyde or ketone as illustrated by the proposed mechanism (9):



When the intermediate zwitterion is stabilized by a protic solvent, ketal-type peroxides are formed, e.g., alcohol offers ether-hydroperoxides and acid offers ester-hydroperoxides. The zwitterion can undergo other reactions like polymerization, rearrangement or reaction with an aldehyde or ketone. The reader is referred to the excellent review by Bailey (9) for an extensive presentation of ozone reactions.

#### Analysis

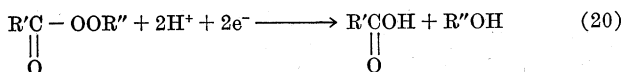
The structure of peroxides influences chemical reactivity and physical properties of the peroxy group. Three of the more important analytical techniques in use for peroxide determinations are iodometry, polarography, and infrared spectrometry, each of which reveals the influence of structure surrounding the -O-O- group.

##### Iodometry

The procedure involves reacting a peroxide in a solvent containing iodide ion and titrating the liberated iodine with standard sodium thiosulfate solution. One mole of peroxide stoichiometrically liberates one mole of iodine. Many variations in iodometry have been developed for the quantitative determination of different types of peroxides. In general, acetic acid, isopropyl alcohol, and acetone are the more important solvents with sodium iodide, potassium iodide or hydriodic acid providing the iodide source. Dialkyl peroxides and *t*-butyl peroxy esters react very slowly, indeed, requiring iron salts as catalytic agents to accelerate their reaction (1a,40). The order of increasing reactivity of different peroxides with iodide to form iodine has been found to be di-*t*-butylperoxides < trimeric ketone peroxides < dialkyl peroxides and dimeric ketone peroxides < *t*-butyl peresters < hydroperoxides < diacyl peroxides < peracids (41).

##### Polarography

Polarography is a versatile electrometric method that offers one of the best techniques for peroxide analysis (1o). The reductions are 2-electron reactions that lead to rupture of the -O-O- bond to form OH groups, for example,



The half-wave potentials,  $E_{1/2}$ , among other factors, depend on structure and relate to the bond strength of the group being reduced. The more negative the  $E_{1/2}$ , the more difficult is the reduction. Di-*t*-butyl peroxide is not reduced over the normal polarographic range. For an aliphatic peroxide series having saturated alkyl chains exceeding two carbon atoms, the order of decreasing bond strength based on  $E_{1/2}$  (42) is correlated to be

	di- <i>t</i> -butyl peroxide>	dialkyl peroxides>	<i>t</i> -butyl peresters>
$-E_{1/2}$ (volt vs. S.C.E.)	> 2	> 1	0.8-1.0
$E_A$ (kcal/mole)	38-40	36-37	35-36
	hydroper- oxides>	diacyl peroxides>	peracid
$-E_{1/2}$ (volt vs. S.C.E.)	0.6-0.9	0.10	0.00-0.06
$E_A$ (kcal/mole)	27-32	30	24

which approximately parallels the activation energies (43) obtained for their decompositions.<sup>2</sup> It should be noted that this order also follows their reactivity with iodide ion.

#### Infrared

The peroxide chemist is partly handicapped when he uses infrared spectroscopy as a diagnostic tool for peroxide analysis. This arises from the fact that, because the stretching mode of the  $-\text{O}-\text{O}-$  group is not associated with any great change in dipole moment, it shows a weak vibrational absorption in the infrared. Also, because masses and force constants of the  $-\text{O}-\text{O}-$  group are so similar to those of  $\text{C}-\text{O}$  and  $\text{C}-\text{C}$ , any characteristic frequency may be obscured by the latter's presence as shown by the oxirane function which absorbs in the same region. Nevertheless, a sufficient number of peroxides have been studied to demonstrate an  $\text{O}-\text{O}$  vibrational absorption by most peroxides in the spectral region of  $952\text{ cm}^{-1}$  ( $10.5\text{ }\mu$ ) to  $833\text{ cm}^{-1}$  ( $12\text{ }\mu$ ).

The molecular environment can influence the characteristic frequency of groups, as shown by shifts in frequency. Even though the  $-\text{O}-\text{O}-$  vibrational frequency may be obscured in the spectra or absent altogether, the peroxy group influences the frequencies of such adjacent groups as carbonyl and hydroxyl when present. The spectra of these compounds are often sufficiently different from their nonperoxidic analogs to be useful in diagnosis.

The structure of hydrogen peroxide has been found to be skewed in which one  $\text{O}-\text{O}-\text{H}$  plane is approximately perpendicular to the other  $\text{O}-\text{O}-\text{H}$  plane (44). Dipole moment studies recently conducted on representative examples of organic peroxides from each class have confirmed retention of this skewed structure (45). Various peroxide types differ somewhat in the dihedral angles (Table II), being lower for peracids ( $72^\circ$ ), due to hydrogen-bonding and slightly higher for di-*t*-butyl peroxide ( $123^\circ$ ) due to

steric hindrance.<sup>3</sup> The dipole moment resulting from the skew would lead one to expect a vibrational absorption band in the infrared for the  $-\text{O}-\text{O}-$  group.

**O-O:** The  $\text{O}-\text{O}$  stretching frequency has been definitely identified at  $877\text{ cm}^{-1}$  ( $11.4\text{ }\mu$ ) for hydrogen peroxide and deuterium peroxide (44). This frequency has been calculated to be  $883\text{ cm}^{-1}$  ( $11.3\text{ }\mu$ ) for hydroperoxides (46) and  $985\text{--}819\text{ cm}^{-1}$  ( $10.15\text{--}12.21\text{ }\mu$ ) for dialkyl peroxides (47). Table II lists some of the pertinent measurements that have been obtained on aliphatic peroxides.

Peracids show a broad band of medium intensity at about  $865\text{ cm}^{-1}$  ( $11.56\text{ }\mu$ ) which is absent in the corresponding carboxylic acids (48).

Hydroperoxides show a weak absorption at  $877\text{ cm}^{-1}$  ( $11.4\text{ }\mu$ ) to  $847\text{ cm}^{-1}$  ( $11.8\text{ }\mu$ ). This is a region in which the corresponding alcohols also absorb, prohibiting its use as a unique means for hydroperoxide characterization (49).

TABLE II  
Dihedral Angles and I. R. Absorption Data for Peroxides<sup>a</sup>

	Dihedral angle	$\text{O}-\text{O},\text{ cm}^{-1}$	$\text{C}=\text{O},\text{ cm}^{-1}$	$\text{OH}$ and $\text{OOH}^b,\text{ cm}^{-1}$
$\text{H}_2\text{O}_2$	$120^\circ$	877	.....	3560
Peracid	$72^\circ$	865	1748	6850, 4830, 3530, 3280, 947
Hydro- peroxides	$100^\circ$	883 (calcd) 877-847 (obsd)	.....	6850, 4830, 3550, 3390, 877-847
Dialkyl peroxides	$123^\circ$ (di- <i>t</i> -Bu) $105^\circ$ ( <i>t</i> -Bu, <i>n</i> -Bu)	985-819 (calcd) ~877 (obsd)	.....	.....
<i>t</i> -Bu-per- ester	$100\text{--}165^\circ$	855	1770	.....
Diacyl peroxides	$\sim 100^\circ$	892	doublet { 1775, longer 1803	.....

<sup>a</sup> See text for references and discussion.

<sup>b</sup> Only the important absorptions are listed.

Only a few low mol wt, simple aliphatic members of dialkyl peroxides have been experimentally subjected to infrared analysis. For diethyl peroxide one band at  $11.4\text{ }\mu$  ( $877\text{ cm}^{-1}$ ) replaces two in diethyl ether at  $11.6\text{ }\mu$  ( $862\text{ cm}^{-1}$ ) and  $11.8\text{ }\mu$  ( $847\text{ cm}^{-1}$ ) (47). Minkoff assigned this frequency, with reservations, to the  $-\text{O}-\text{O}-$  stretching vibration on the basis of certain evidence that he cited. Perfluorodimethyl peroxide ( $\text{CF}_3\text{OOCF}_3$ ) shows a medium band at about  $885\text{ cm}^{-1}$  ( $11.3\text{ }\mu$ ) (50). Di-*t*-butyl peroxide has a strong band at  $874\text{ cm}^{-1}$  ( $11.44\text{ }\mu$ ) while *t*-butyl hydroperoxide has a medium strength band at this frequency and a more intense one at  $847\text{ cm}^{-1}$  ( $11.8\text{ }\mu$ ) (51,52,53). These bands for *t*-butyl peroxides and non-peroxy analogs have been assigned to the *t*-butoxy group (52,53). The large dihedral angle for di-*t*-butyl peroxide imposes a higher degree of planarity in this molecule which decreases the intensity of the  $\text{O}-\text{O}$  stretching vibration (due to a lower dipole moment) leaving primarily the characteristic *t*-butyl group modes.

No spectra are available for normal and secondary alkyl peresters. *t*-Butyl peresters of long-chain fatty acids reveal two bands, one at about  $855\text{ cm}^{-1}$  ( $11.7\text{ }\mu$ ) of medium intensity and a second weak, broad band at  $920\text{ cm}^{-1}$  ( $10.9\text{ }\mu$ ) (53,54). The corresponding *t*-butyl esters also have a similar pair of bands in this region,

<sup>2</sup> Disagreement in published values for energies of activation for many of these peroxides and reliable first-order decomposition measurements still required for hydroperoxides and peroxyacids permits only an approximate correlation of activation energy with half-wave potential. Primary and secondary hydroperoxides have not been studied under conditions by which second-order decomposition has been completely eliminated. Peroxyacids decompose by two routes: (a)  $\text{O}-\text{O}$  fission of peroxyacid into  $\text{RCO}\cdot$  and  $\text{HO}\cdot$  radicals (70) and (b) decom-

position by a route that leads to fatty acid and oxygen (70). The energies of activation for these two decomposition modes are expected to differ significantly. The reported value is a composite one, but relates mainly to route (b).

<sup>3</sup> The recent reported change in the dihedral angle of hydrogen peroxide from  $95^\circ\text{--}120^\circ$  (44) suggests that the dihedral angle of organic peroxides also requires further refinement.

a weak, broad band at  $845\text{ cm}^{-1}$  ( $11.8\text{ }\mu$ ) and a medium one at  $948\text{ cm}^{-1}$  ( $10.55\text{ }\mu$ ) (53,54). *t*-Butyl peresters and esters can then be differentiated from each other, and distinguished from normal alkyl esters which show only a trace of a doublet in this region. The  $855\text{ cm}^{-1}$  band has been attributed to the *t*-butoxy group rather than to the  $\text{—O—O—}$  vibration (53,54).

Diacyl peroxides show a medium semi-broad band at  $892\text{ cm}^{-1}$  ( $11.2\text{ }\mu$ ) in contrast to anhydrides which have a weak, very broad band at  $925\text{ cm}^{-1}$  ( $10.8\text{ }\mu$ ) (51,54,55).

The evidence is in favor of an  $\text{—O—O—}$  vibrational absorption appearing between  $900\text{ cm}^{-1}$  ( $11.1\text{ }\mu$ ) and  $850\text{ cm}^{-1}$  ( $11.8\text{ }\mu$ ) but this absorption is obscured by *t*-butoxy, alcohol, and oxirane absorptions which also appear in this region.

**C=O:** The strong, single carbonyl band for peracids at  $1748\text{ cm}^{-1}$  ( $5.72\text{ }\mu$ ) does not change on dilution. Swern and associates found no unbonded carbonyl under any of the conditions they studied (48). Carboxylic acids in solution have a strong carbonyl absorption at  $1710\text{ cm}^{-1}$  for the dimeric hydrogen-bonded carbonyl and a weak monomeric band at  $1760\text{ cm}^{-1}$  (56).

*t*-Butyl peresters have a sharp carbonyl band at  $1770\text{ cm}^{-1}$  (53,54) (Davison reports  $1783\text{ cm}^{-1}$  for peracetate) (57). This band is clearly defined with respect to the corresponding  $1720\text{ cm}^{-1}$  band of the analogous *t*-butyl esters (53,54).

Diacyl peroxides have a doublet at  $1775\text{ cm}^{-1}$  and  $1803\text{ cm}^{-1}$  [Davison (57) reports  $1785$  and  $1812\text{ cm}^{-1}$ ; Bellamy et al (58) report  $1777$  and  $1806\text{ cm}^{-1}$ ] the lower frequency band being the stronger and sharper. Diacyl anhydrides have a doublet at  $1748$  and  $1813\text{ cm}^{-1}$ , the higher frequency band being the stronger and sharper (54,58). The larger frequency split for anhydrides ( $60\text{ cm}^{-1}$ ) which is about  $2\frac{1}{2}$  times that for the peroxides ( $25\text{ cm}^{-1}$ ), results from its shorter coupling link.

**OH:** A sharp OH band occurs at  $3280\text{ cm}^{-1}$  ( $3.05\text{ }\mu$ ) for peracids. Intramolecular hydrogen-bonding is indicated since this band does not change on dilution and the shift of OH parallels the shift of C=O (48). In dilute solution carboxylic acids show not only the strong, broad dimer band but also a sharp unassociated OH band at  $3530\text{ cm}^{-1}$  ( $2.83\text{ }\mu$ ). Similarly alcohols in dilute solution show both the associated ( $3340\text{ cm}^{-1}$ ) and unassociated ( $3635\text{ cm}^{-1}$ ) hydroxyl bands. Carboxylic acids have a strong, broad deformation mode at  $940\text{ cm}^{-1}$  while peracids show a weaker mode at  $947\text{ cm}^{-1}$ .

Hydrogen-bonded hydroperoxides and alcohols possess nearly identical O—H stretching vibration (49). To illustrate the hydrogen-bonded OH, the average wave length for 18 examples is  $2.95\text{ }\mu$  ( $3390\text{ cm}^{-1}$ ) for ROOH compared to  $2.99\text{ }\mu$  ( $3345\text{ cm}^{-1}$ ) for ROH, an average shift of  $0.04\text{ }\mu$  ( $45\text{ cm}^{-1}$ ) (49). In all of the cases reported by Williams and Mosher, alcohols had the longer wave length suggesting stronger hydrogen-bonding.

The near-infrared region offers an excellent location for distinguishing hydroperoxides from both alcohols and other peroxides (59). The fundamental O—H stretching vibration for free OOH at  $2.82\text{ }\mu$  ( $3546\text{ cm}^{-1}$ ) is difficult to differentiate from other stretching fundamentals and carbonyl overtones. Hydroperoxides in dilute solution, however, have one band at  $1.46\text{ }\mu$  ( $6849\text{ cm}^{-1}$ ) [a harmonic of the fundamental at  $2.82\text{ }\mu$  ( $3546\text{ cm}^{-1}$ )] and one at  $2.07\text{ }\mu$

( $4831\text{ cm}^{-1}$ ) (probably a combination absorption) which are distinguishable from other bands in the region.

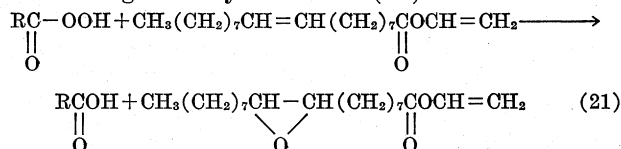
A few examples should suffice to show the utility of infrared spectroscopy to the peroxide chemist. Raley used the absorption at  $873\text{ cm}^{-1}$  for estimating di-*t*-butyl peroxide in the presence of *t*-butanol (60), and Bartlett and Hiatt followed the decomposition of *t*-butyl peresters by observing the change in the carbonyl region (61). The near-infrared absorption for  $\text{—O—O—H}$  serves to measure formation of hydroperoxide in autoxidation of fatty oils (59). Our laboratory has found both the  $\text{—O—O—}$  vibrational band at  $892\text{ cm}^{-1}$  ( $11.2\text{ }\mu$ ) and the C=O doublet useful for following decompositions and reactions of diacyl peroxides (54).

## Reactions

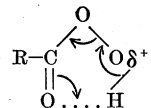
The reactions presented here are representative examples demonstrating the versatility of peroxides as reagents and as intermediates for conversion to other compounds.

### Epoxidation

**Peroxy Acid Epoxidation:** Peroxy acids oxidize double bonds to the oxirane derivative (1n). The rate of oxidation depends on the type of double bond being attacked. In the following illustration, the internal double bond of vinyl oleate is oxidized about 220 times faster than the double bond of the vinyl ester group which is deactivated by the electron-withdrawing carboxyl function (62).

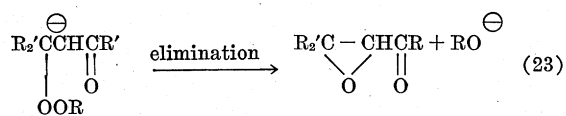
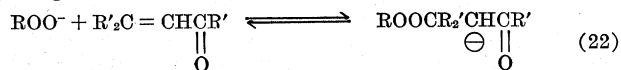


This difference in rate permits a specific epoxidation. Peroxy acids are electrophilic in character (electron deficient as illustrated in the cyclic structure



for peracids) requiring a relatively electron-rich double bond center for the rate to be reasonably rapid.

**Hydroperoxide Epoxidation:** Double bonds deactivated by carbonyl functions either react too slowly or undergo no reaction with peroxy acids. Epoxidations of  $\alpha,\beta$ -unsaturated ketones have been achieved by alkaline hydroperoxide oxidation which proceed through a Michael type addition (63).

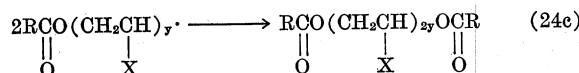
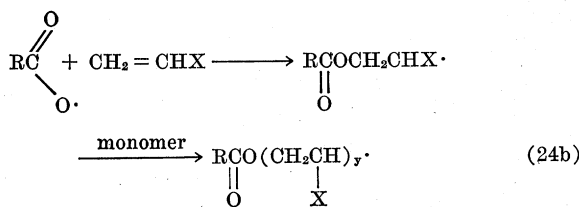
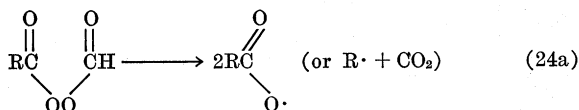


In contrast to the peroxy acid epoxidation, this Michael type is a nucleophilic attack on the electron-deficient beta carbon of the double bond alpha, beta to the carbonyl.

### Polymerization Initiators

Peroxides decompose to free radicals capable of initiating polymerization of unsaturated monomers

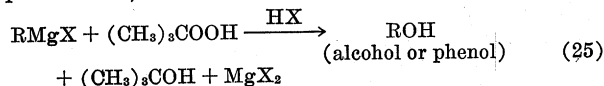
such as vinyl chloride and vinyl esters schematically represented in the following sequence (64):



Lauroyl peroxide, a peroxide based on fat sources, is an important polymerization initiator.

#### Grignard Reaction on Peroxides

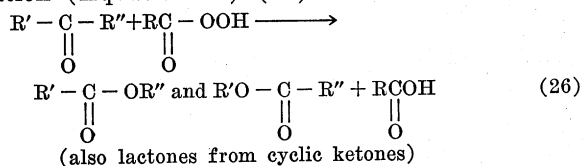
Reaction of Grignard reagents with peroxides (65) offers a new route to alcohols, phenols, and ethers (Equation 25).



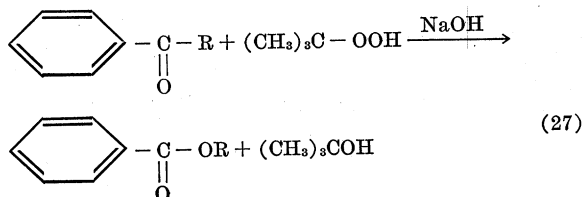
This type of reaction is unique for the preparation of t-butyl ethers.

#### Oxidation of Ketones to Esters

Two types of ketone oxidations leading to ester formation may be illustrated. The first employing peroxy acid as oxidant is called the Baeyer-Villiger oxidation (Equation 26) (66).



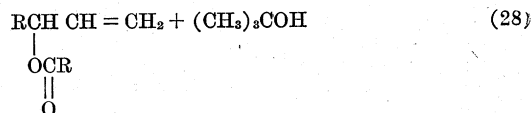
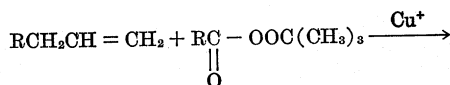
The second, employing hydroperoxide in basic media cleaves the C-C linkage between the carbonyl carbon and aliphatic carbon but not between carbonyl carbon and aromatic carbon (Equation 27) (67).



This latter reaction is more selective than the Baeyer-Villiger but yields are lower.

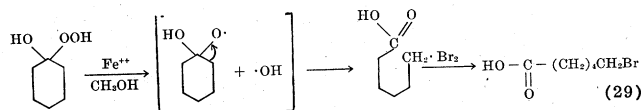
#### Peroxide-Metal Reactions

Metal-Catalysis: Kharasch and his associates (68) have found that reaction between peroxides and olefins catalyzed by polyvalent metal ions gives derivatives substituted largely (85-90%) on the carbon alpha to the double bonds (Equation 28). This reac-



tion offers an alternative to the N-bromosuccinimide reaction for introducing a substituent alpha to the double bond.

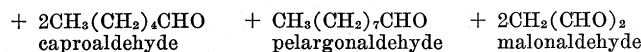
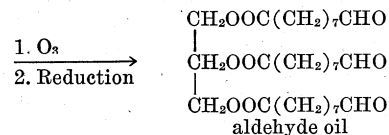
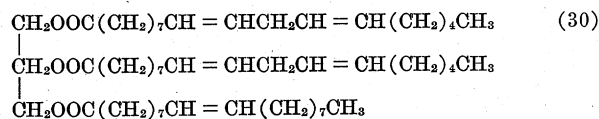
Redox: An interesting example of an oxidation-reduction between peroxides and metal ion has been reported for the preparation of  $\alpha,\omega$ -substituted derivatives from cyclic ketone peroxides (69).



The ferrous iron is used in excess of stoichiometric quantities which contrasts this reaction with the previous catalytic one.

#### Ozonization of a Fatty Oil

Ozonization of soybean oil followed by *reductive decomposition of the ozonolysis products* yields a polyaldehydic product termed "aldehydic oil" (71). The reaction is illustrated in Equation 30 for an idealized triglyceride structure for soybean oil.



The polyfunctional aldehyde oil offers an intriguing condensation polymer intermediate capable of undergoing condensation reactions with phenolic compounds, urea, amines, and polyols to give cross-linked polymers.

This paper has attempted to demonstrate the range of properties possessed by peroxides as a consequence of their unique structure. They are decomposed by thermal, photochemical, and catalytic means. It is interesting to note that their stabilities also range from the shock sensitive, explosive dimethyl peroxide ( $\text{CH}_3\text{O}-\text{O}-\text{CH}_3$ ) to the extremely stable perfluorodimethyl peroxide ( $\text{CF}_3\text{O}-\text{O}-\text{CF}_3$ ) which is, in fact, synthesized at 287°C (50). The versatility of reactions shown by organic peroxides promises a bright future for their participation in synthetic organic chemistry including, hopefully, in the chemurgy of fats.

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